

CLAIMS

What is claimed is:

1. A perfluoropolyether comprising perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and a 1,2-bis(perfluoromethyl)ethylene diradical,  $-\text{CF}(\text{CF}_3)\text{CF}(\text{CF}_3)-$ , is absent in the molecule of said perfluoropolyether.
2. A perfluoropolyether according to claim 1 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.
3. A perfluoropolyether according to claim 1 wherein said perfluoropolyether has the formula of  $\text{C}_r\text{F}_{(2r+1)}-\text{A}-\text{C}_r\text{F}_{(2r+1)}$ ; each  $r$  is independently 3 to 6; if  $r = 3$ , both end groups  $\text{C}_r\text{F}_{(2r+1)}$  must be a propyl radical; A is selected from the group consisting of  $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_w$ ,  $\text{O}-(\text{C}_2\text{F}_4-\text{O})_w$ ,  $\text{O}-(\text{C}_2\text{F}_4-\text{O})_x(\text{C}_3\text{F}_6-\text{O})_y$ ,  $\text{O}-(\text{CF}_2\text{CF}_2\text{CF}_2-\text{O})_w$ ,  $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_x(\text{CF}_2\text{CF}_2-\text{O})_y-(\text{CF}_2-\text{O})_z$ , and combinations of two or more thereof;  $w$  is 4 to 100; and  $x$ ,  $y$ , and  $z$  are each independently 1 to 100.
4. A composition comprising a perfluoropolyether, which comprises perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and 1,2-bis(perfluoromethyl)ethylene diradical,  $-\text{CF}(\text{CF}_3)\text{CF}(\text{CF}_3)-$ , is absent in the molecule of said perfluoropolyether.
5. A composition according to claim 4 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.
6. A composition according to claim 4 wherein said perfluoropolyether has the formula of  $\text{C}_r\text{F}_{(2r+1)}-\text{A}-\text{C}_r\text{F}_{(2r+1)}$ ; each  $r$  is independently 3 to 6; if  $r = 3$ , both end groups  $\text{C}_r\text{F}_{(2r+1)}$  must be a propyl radical; A is selected from the group consisting of  $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_w$ ,  $\text{O}-(\text{C}_2\text{F}_4-\text{O})_w$ ,  $\text{O}-(\text{C}_2\text{F}_4-\text{O})_x(\text{C}_3\text{F}_6-\text{O})_y$ ,  $\text{O}-(\text{CF}_2\text{CF}_2\text{CF}_2-\text{O})_w$ ,  $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_x(\text{CF}_2\text{CF}_2-\text{O})_y-(\text{CF}_2-\text{O})_z$ , and combinations of two or more thereof;  $w$  is 4 to 100; and  $x$ ,  $y$ , and  $z$  are each independently 1 to 100.

7. A composition according to claim 4 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

8. A composition according to claim 5 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

9. A composition according to claim 6 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

10. A composition according to claim 9 wherein said thickener is selected from the group consisting of poly(tetrafluoroethylene), fumed silica, and boron nitride, and combinations of two or more thereof.

11. A process for producing a perfluoropolyether comprising (1) contacting a reactant with a metal halide to produce an alkoxide wherein said reactant is selected from the group consisting of a perfluoro acid halide, a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide, a C<sub>3+</sub> fluoroketone, and combinations or two or more thereof; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to its corresponding alcohol; (5) converting said corresponding alcohol with a base to a salt; (6) contacting said salt with a C<sub>3+</sub> olefin or perfluoroalkene to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

12. A process according to claim 11 wherein said C<sub>3+</sub> olefin is a C<sub>3</sub>-C<sub>6</sub> straight chain olefin, C<sub>3</sub>-C<sub>6</sub> branched chain olefin, C<sub>3</sub>-C<sub>6</sub> allyl halide, or combinations of two or more thereof.

13. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting

said salt with a C<sub>3</sub> or higher olefin to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

14. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting said salt with a C<sub>3+</sub> branched fluoroalkene or a C<sub>3+</sub> allyl halide to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

15. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

16. A process according to claim 11 wherein said process comprises (1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

17. A process according to claim 11 wherein said process comprises (1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting said salt with a C<sub>3+</sub> olefin to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

18. A process according to claim 11 wherein said process comprises  
(1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide;  
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane  
to produce a second acid halide; (3) esterifying said second acid halide to an ester;  
5 (4) reducing said ester to its corresponding alcohol; (5) converting said  
corresponding alcohol with a base to a salt; (6) contacting said salt with a C<sub>3+</sub>  
fluoroalkene to produce a fluoropolyether; and (7) fluorinating said  
fluoropolyether.

19. A process according to claim 11 wherein said process comprises  
10 (1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with  
a metal halide to produce an alkoxide; (2) contacting said alkoxide with  
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;  
(3) contacting said second acid halide with a metal iodide to produce a second  
iodide; (4) fluorinating said second iodide.

15 20. A process according to claim 11 wherein said process comprises  
(1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide;  
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane  
to produce an acid halide; (3) contacting said acid halide with a metal iodide to  
produce a second iodide; (4) fluorinating said second iodide.

20 21. A process according to claim 11 wherein said process comprises  
(1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with  
a metal halide to produce an alkoxide; (2) contacting said alkoxide with  
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;  
(3) contacting said second acid halide with a metal iodide to produce a second  
25 iodide; (4) contacting said second iodide with an olefin to produce a third iodide;  
and (5) fluorinating said third iodide.

22. A process according to claim 11 wherein said process comprises  
(1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide;  
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane  
30 to produce an acid halide; (3) contacting said acid halide with a metal iodide to  
produce a second iodide; (4) contacting said second iodide with an olefin to  
produce a third iodide; and (5) fluorinating said third iodide.

23. A process according to claim 11 wherein said process comprises  
(1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with  
a metal halide to produce an alkoxide; (2) contacting said alkoxide with  
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;  
5 (3) contacting said second acid halide with a metal iodide to produce a second  
iodide; (4) contacting said second iodide with an olefin to produce a third iodide;  
(5) dehydrohalogenating said third iodide to give a second olefin; and (6)  
fluorinating said second olefin.

24. A process according to claim 11 wherein said process comprises  
10 (1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide;  
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane  
to produce an acid halide; (3) contacting said acid halide with a metal iodide to  
produce a second iodide; (4) contacting said second iodide with an olefin to  
produce a third iodide; (5) dehydrohalogenating said third iodide to give a second  
15 olefin; and (6) fluorinating said second olefin.

25. A process according to claim 11 wherein said process comprises  
fluorinating a fluoropolyether having alkyl radical end groups; said radical has at  
least 3 carbon atoms per radical and is substantially free of methyl and ethyl; and  
a 1,2-bis(methyl)ethylene diradical, -CH(CH<sub>3</sub>)CH(CH<sub>3</sub>)-, is absent in the  
20 molecule of said fluoropolyether .

26. A process according to claim 25 wherein said process is carried out  
in the presence of a mixture comprising an inert solvent and a hydrogen fluoride  
scavenger.

27. A process according to claim 11 wherein said process comprises  
25 (1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with  
a metal halide to produce an alkoxide; (2) contacting said alkoxide with  
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;  
(3) contacting said second acid halide with a metal iodide to produce a second  
iodide; (4) replacing the iodine radicals of said second iodide with hydrogen  
30 radicals to produce a fluoropolyether containing hydrogen radicals; and (5)  
fluorinating said fluoropolyether.

28. A process according to claim 11 wherein said process comprises  
(1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide;  
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane  
to produce an acid halide; (3) contacting said acid halide with a metal iodide to  
5 produce a second iodide; (4) replacing the iodine radicals of said second iodide  
with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals;  
and (5) fluorinating said fluoropolyether.

29. A process according to claim 11 wherein said process comprises  
(1) contacting a perfluoro acid halide or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with  
10 a metal halide to produce an alkoxide; (2) contacting said alkoxide with  
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;  
(3) contacting said second acid halide with a metal iodide to produce a second  
iodide; (4) contacting said second iodide with an olefin to produce a third iodide;  
(5) replacing the iodine radicals of said second iodide with hydrogen radicals to  
15 produce a fluoropolyether containing hydrogen radicals; and (6) fluorinating said  
fluoropolyether.

30. A process according to claim 11 wherein said process comprises  
(1) contacting a C<sub>3</sub> to C<sub>6</sub> fluoroketone with a metal halide to produce an alkoxide;  
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane  
20 to produce an acid halide; (3) contacting said acid halide with a metal iodide to  
produce a second iodide; (4) contacting said second iodide with an olefin to  
produce a third iodide; (5) replacing the iodine radicals of said second iodide with  
hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and  
(6) fluorinating said fluoropolyether.

25 31. A process according to claim 11 wherein said process comprises  
(1) contacting a perfluoro acid halide, a C<sub>3</sub> to C<sub>6</sub> fluoroketone, or a C<sub>2</sub> to C<sub>4</sub>-  
substituted ethyl epoxide with a metal halide to produce an alkoxide; (2)  
contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to  
produce a second acid halide; (3) esterifying said second acid halide to an ester;  
30 (4) reducing said ester to an alcohol; (5) contacting said alcohol with sulfur  
tetrafluoride or derivative thereof to convert the OH groups of said alcohol to

fluorine radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

32. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide, a C<sub>3</sub> to C<sub>6</sub> fluoroketone, or a C<sub>2</sub> to C<sub>4</sub>-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a phosphorus pentahalide or derivative thereof to convert the OH groups of said alcohol to halide radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

33. A process according to claim 11 wherein said process comprises (1) contacting a fluorotertiary alkoxy-containing compound with a first fluoropolyether to produce a second fluoropolyether and optionally (2) fluorinating said second fluoropolyether wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol or a perfluoro-t-butyl hypofluorite; said first fluoropolyether has (i) a starting C<sub>3</sub>-C<sub>6</sub> segment or R<sub>f</sub><sup>8</sup>(R<sub>f</sub><sup>9</sup>)CFO segment and (ii) a -A-O-C(CF<sub>3</sub>)=CF<sub>2</sub> or a -A-O-C(CF<sub>3</sub>)=CHF intermediate end group; R<sub>f</sub><sup>8</sup> is C<sub>j</sub>F<sub>(2j+1)</sub>; R<sub>f</sub><sup>9</sup> is C<sub>k</sub>F<sub>(2k+1)</sub>; j and k are each ≥ 1; (j + k) ≤ 5; and A is selected from the group consisting of O-(CF(CF<sub>3</sub>)CF<sub>2</sub>-O)<sub>w</sub>, O-(CF<sub>2</sub>-O)<sub>x</sub>(CF<sub>2</sub>CF<sub>2</sub>-O)<sub>y</sub>, O-(C<sub>2</sub>F<sub>4</sub>-O)<sub>x</sub>, O-(C<sub>2</sub>F<sub>4</sub>-O)<sub>x</sub>(C<sub>3</sub>F<sub>6</sub>-O)<sub>y</sub>, O-(CF(CF<sub>3</sub>)CF<sub>2</sub>-O)<sub>x</sub>(CF<sub>2</sub>-O)<sub>y</sub>, O(CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O)<sub>w</sub>, O-(CF(CF<sub>3</sub>)CF<sub>2</sub>-O)<sub>x</sub>(CF<sub>2</sub>CF<sub>2</sub>-O)<sub>y</sub>-(CF<sub>2</sub>-O)<sub>z</sub>, and combinations of two or more thereof.

34. A process according to claim 33 wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol.

35. A process according to claim 33 wherein said fluorotertiary alkoxy-containing compound is a perfluoro-t-butyl hypofluorite.